International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:9, No:12, 2015

Investigation of Utilization Possibility of Fluid Gas Desulfurization Waste for Industrial Waste Water Treatment

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***Abstract*—**Flue gas desulfurization gypsum (FGD) is a waste material arouse from coal power plants. Hydroxyapatite (HAP) is a biomaterial with porous structure. In this study, FGD gypsum which retrieved from coal power plant in Turkey was characterized and HAP particles which can be used as an adsorbent in wastewater treatment application were synthesized from the FGD gypsum. The raw materials are characterized by using X Ray Diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) techniques and produced HAP are characterized by using XRD. As a result, HAP particles were synthesized at the molar ratio of 5:10, 5:15, 5:20, 5:24, at room temperature, in alkaline medium (pH=11) and in 1 hour-reaction time. Among these conditions, 5:20 had the best result.

***Keywords*—**FGD wastes, HAP, gypsum, wastewater.

I. Introduction

CONTINUOUSLY increase in the amount and formation of waste is the huge issue for all over the world. Solid waste storage and industrial waste waters are two of biggest problem for future of the world and natural sources [1]. The irregular storage of solid wastes and dumped in to rivers, seas directly bring a lot of environmental and health problems. In addition to environmental and health effects, evaluation of wastes is also important for economic aspects. Available recourses in the world are decreasing promptly and utilize wastes as a beginning material for production is coming in to prominence [2].

Flue gas desulfurization units in coal power plants are constituted on the purpose of decreasing of SO_x emissions from the coal power plant to the air. In this unit, 95% of SO_x emissions can be captured thereby converted to gypsum material which is called flue gas desulfurization gypsum [3]. Flue gas desulfurization (FGD) gypsum is a waste material produced from desulfurization of flue gases such SO_2 in power stations with really high amounts. FGD gypsum is a common waste which is generated from wet flue gas desulfurization unit of coal power plants which supply energy requirement a lot of countries such as Turkey [4]. The coal which is using in coal power plants contains up to 2.5% of sulfur. In one power station part of flue gas desulfurization unit, FGD gypsum is created up to 20 t/h FGD gypsum is composed mainly $CaSO_4 \cdot 2H_2O$ and this structure allow to see the FGD gypsum as an Ca source for different application [3], [5]. The FGD gypsum is fine grained material with a low moisture content and high specific surface area [6]. Besides, the majority of FGD wastes are storage directly open or closed area and this kind of storage cause to not only air and soil pollution also groundwater pollution. Especially 80 countries on the world host huge amount of FGD gypsum. A little amount of it is utilized for road stabilization, cement industry or as a construction material or gypsum plasterboards [4], [7].

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Hydroxyapatite (HAP) with the $Ca_{10}(PO_4)_6(OH)_2$ composition is a biocompatible and bioactive material. It has chemically similar structure with bones and it has been used for bone tissue and ceramic implants. In addition, it can be used for sewage treatment, biosensor, and catalysis. At the same time some chemical properties of HAP such as specific surface area and porous structure enable to use for different application such as adsorption, removal heavy metals, treatment wastewaters [8], [9].

So many HAP production methods were explained in literature until today. Solid state reaction, co-precipitation, hydrothermal reaction, sol–gel synthesis, microemulsion synthesis and mechano-chemical synthesis methods can be used [10]. Not only chemical starting materials but also natural sources, by-products and wastes can be used for preparing HAP molecules. For instance, bio wastes such as food or agricultural residues, fish scales, dead animal bones, eggshells and corals provide a large area for deriving HAP particles. In addition to biological compounds, industrial wastes and by-products such as natural gypsum, phosphogypsum and flue gas desulfurization waste gypsum can be prefer to prepare HAP particles. Because these waste includes high amount of calcium required for synthesis [11], [12].

The treatment of industrial wastewaters occupies a place in wastewater issue because of its amount and hazardous effects. Especially, wastewaters from chemical, pharmaceutical, electro coating, petroleum, plastic, textile industries include high amount of heavy metals such as Cd, Cr, Cu, Ni, Zn, Pb [2]. Heavy metals can be absorbed by living organisms because they have got high solubility property. When heavy metals are absorbed by any living organisms, it takes a place in food chain and thus, large amount of concentrations of hazardous heavy metals accumulate in the human body and cause serious diseases and fatal results. In addition to direct impact for human body, accumulation of heavy metal in soil causes soil pollution, effect plant and animals [13], [14].

Many methods can be used for cleaning wastewater and removal of heavy metals. Physical, chemical, biological, and advanced treatment methods are developed for this aim. Adsorption is a good option in these methods. Because it is low cost, effective, and easy way to removal, heavy metals and reuse treated wastewaters. A great number of materials can be used as an adsorbent in adsorption process such as active carbon, fly ash, silica gel, zeolites, metal oxides etc. In addition, hydroxyapatite is effective and common adsorbent with porous structure, specific surface properties, being a low cost material, lower solubility in a large range of pH and high efficiency for heavy metals loading [2].

In this study, the industrial waste material FGD gypsum which is low cost and common waste was used for synthesis of HAP thereby studying different ratios of raw materials and setting conditions. Raw materials were characterized by X-ray diffraction (XRD) and Fourier transforms infrared spectroscopy (FT-IR) techniques, and synthesized HAP particles were characterized by XRD. Synthesized HAP material was analyzed on the purpose of using heavy metal removal from the industrial wastewaters. Thus bring a solution possibility both solid and liquid waste issue is investigated.

II. Materials and Methods

A. Raw Materials Preparation

FGD gypsum waste was supplied from Çayırhan Coal Power Plant, Ankara-Turkey (Fig. 1). Phosphoric acid (85%, Merck Chemicals) and ammonia solution (25%, Merck chemicals) was used without pretreatment for synthesis.

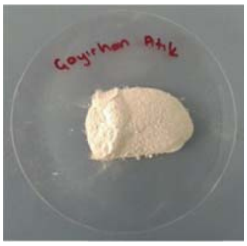

Fig. 1 FGD gypsum waste

Fig. 2 Agate Mortar

Waste FGD gypsum was washed with distilled water several times and was dried at 105°C during 24 hours. Afterwards, dried FGD gypsum was grinded by the help of mortar (Fig. 2) to crush into powder and provide uniformity.

Philips PANalytical XRD (Fig. 3) was preferred for characterization step. In addition to XRD analysis, Perkin Elmer Brand FT-IR technique with Universal ATR sampling accessory – Diamond / ZnSe Crystal was used. Measurement range was selected as 4000–650 cm^{-1}, scan number was 4 and resolution set as 4 cm^{-1} (Fig. 4). Pure ammonia solution was added as an agent for the pH arrangement.

Fig. 3 Philips PANalytical XRD

Fig. 4 Perkin Elmer Spectrum One FT-IR Spectrometer

B. Synthesis of HAP Particles

The simple method was used based on Mousa et al. [9]. Grinded FGD gypsum waste was mixed with distilled water when using vigorous stirring (500 rpm) at room temperature for enough time. Different mole ratios (10, 15, 20 and 24 mole) of phosphoric acid was added slowly. Mole ratios were specified based on the basic reaction which is given in (1). pH was arranged at 11 with ammonia solution. Reaction time was selected as 1 hour.

$$5CaSO_4 2H_2O + 3H_3PO_4 \longrightarrow Ca_5(PO_4)_3OH + 5H_2SO_4 + 9H_2O \quad (1)$$

In the following step, solution was filtered using vacuum filtration and the resulted powder was dried at 80°C for 24 h.

C. Characterization of Raw Materials and Products

FGD gypsum waste and synthesized HAP molecules were grinded using a mortar and powdered before the characterization process. Both the structure of FGD gypsum waste and produced HAP molecules were characterized by XRD (Philips PANalytical, Xpert-Pro). Furthermore, FT-IR equipment (Perkin Elmer, Spectrum One) was used to identify the functional groups present in the products and waste material.

III. Results and Discussion

A. Raw Material Characterization

XRD analysis results of raw material were given Fig. 5 and Table I respectively.

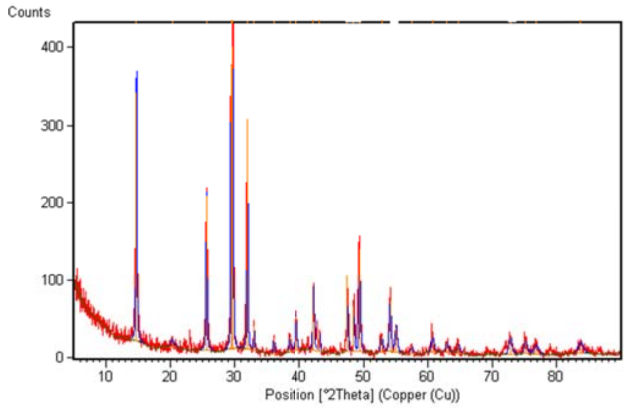

Fig. 5 XRD pattern of FGD gypsum waste

TABLE I
XRD Results of Raw Materials

Reference Code	Compound Name	Chemical Formula	Score
00-033-0310	Bassanite	$CaSO_4 0.5H_2O$	75
00-001-0837	Calcite	$CaCO_3$	49

From the waste FGD gypsum XRD pattern, the major peaks represents 00-033-0310 numbered powder diffraction file (pdf) bassanite ($CaSO_4 0.5H_2O$) also some calcite($CaCO_3$) minor peaks are observed with powder diffraction number of 00-001-0837. Additionally, a little amount of fly ash, carbon grains and anhydrite $CaSO_4$ are observed as trace compounds in line with previous studies [13], [15]. Also, it can be seen in Table I that waste raw material contains a large amount of calcite minerals beside bassanite. It is suitable with expectations because raw material was obtained from a desulfurization process using $CaCO_3$ for providing transform from SO_x to $CaSO_4$. Not only presence of bassanite but also calcite is appropriate provide a Ca source which required for synthesis.

FT-IR spectrum of the waste FGD gypsum is shown in Fig. 6 and FT-IR peak interpretations is given in Table II. The adsorption bands at 3604, 3547, 2162, 1618, 1427, 1134, 1106, 1082, 1006, 874 and 658 cm^{-1} are observed. The bands at 3604 and 3547 cm^{-1} belong to H_2O stretching bands and OH bending of bassanite. H_2O bending modes can be seen at 1618 cm^{-1}. Intensive peaks between at 1006 and 1134 cm^{-1} explain the SO_4 vibration bands. The peak at 874 cm^{-1} characterizes CO_3 groups. The final peak at 658 cm^{-1} is the main characteristic peak of $CaSO_4$.

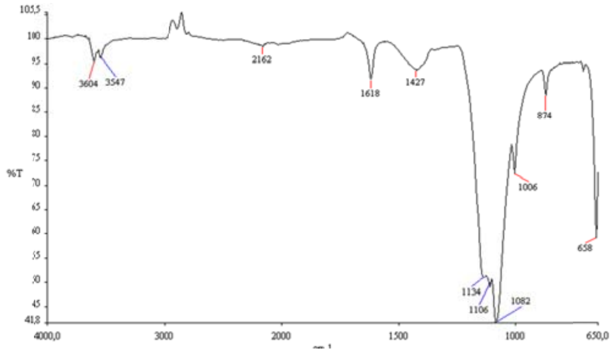

Fig. 6 FT-IR Spectrum of FGD gypsum waste

TABLE II
FT-IR Peak Interpretations

Peaks (cm^{-1})	**Peak Interpretation**
3604	H-O-H stretching
3547	Bending OH
1618	Bending H-O-H
1006-1134	SO_4 asymmetric stretching
874	CO_3 stretching
658	Characteristic peak of $CaSO_4$

B. Synthesized Hydroxyapatite (HAP) XRD Results

The basic reaction equation in given (1) was considered to production of HAP. However, this equation was adopted in keeping with raw materials XRD analysis result which indicates bassanite structure with 0.5 mole H_2O.

XRD patterns of synthesized HAP molecules are shown in the Fig. 7. XRD results of synthesized HAP molecules are given by Table III. From the XRD results obtained it is seen that '00-001-1018' pdf numbered 'Hydroxyapatite' particles were found at all the reactions which includes different molar ratios. Peaks are observed between $2\theta = 20°$ and $40°$ indicate to HAP structure. From the XRD patterns the major peaks represents hydroxyapatite particles. The highest hydroxyapatite formations were seen at the 5:20 molar ratio. The yield of reaction increases until the molar ratio 5:20 and reaches the highest level at the 5:20 molar ratio. After that, sharp decreasing and formation of $CaSO_4$ at $2\theta = 20°$ can be seen easily.

TABLE III
XRD Results of Synthesized HAP molecules

Molar Ratio ($CaSO_4 0.5H_2O$: $H3PO_4$)	**Reference code**	**Compound Name**	**Compound Formula**	**Score**
5:10	00-001-1008	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	38
5:15	00-001-1008	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	45
5:20	00-001-1008	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	50
5:24	00-001-1008	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	27

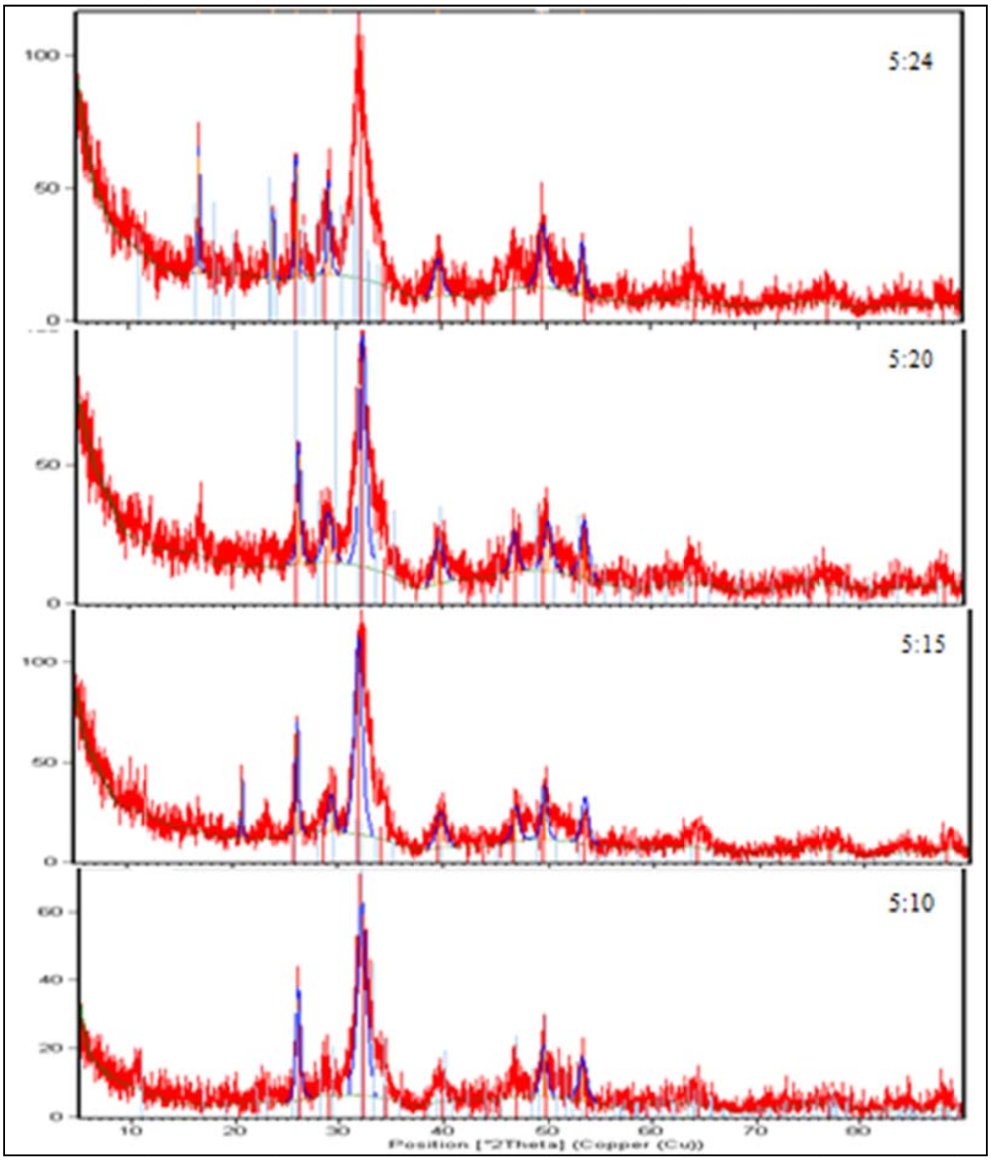

Fig.7 XRD patterns of synthesized HAP molecules

IV. CONCLUSION

Utilization of waste is an important issue depending on increasing industrial activities all over the world. In additionally, storage of wastes is another serious problem. The usage of wastes as a raw or beginning material provides a chance for decreasing cost of raw materials and energy. Also serious problems caused by high amount of waste and improper storage can be decreasing thereby using wastes. Therefore, in this study, flue gas desulfurization gypsum waste was used as a raw material in the production of hydroxyapatite particles. From the result of this study, it is seen that FGD gypsum waste can be used in the production of HAP at room temperature, 1 hour reaction time, under 500 rpm stirring and pH = 11 .According to analysis results the reaction yield can be different based on different molar ratios. The optimum molar ratio is determined as molar ratio of $CaSO_4 0.5H_2O$: H_3PO_4 5:20. At the future studies, reaction time and temperature changes will be search in the synthesis of HAP. Then, heavy metal adsorption from wastewaters using synthesis HAP will be investigated.

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